

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> : <b>C08J 9/14 // C08L 75:04</b>		A1	(11) International Publication Number: <b>WO 94/25514</b>
			(43) International Publication Date: 10 November 1994 (10.11.94)
 (21) International Application Number: PCT/EP94/00642 (22) International Filing Date: 4 March 1994 (04.03.94)  (30) Priority Data: 9308449.9 23 April 1993 (23.04.93) GB 9315130.6 20 July 1993 (20.07.93) GB  (71) Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors: DE VOS, Rik; Valleilaan 40a, B-3110 Rotselaar (BE). BIESMANS, Guy; Nieuw Overlaar 10 - bus 6, B-3300 Tienen (BE). (74) Agents: SWINNEN, Anne, Marie et al.; ICI Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).			
 <b>Published</b> <i>With international search report.</i>			

**(54) Title:** PROCESS FOR PREPARING RIGID POLYURETHANE FOAMS**(57) Abstract**

Process for the preparation of a rigid polyurethane or urethane-modified polyisocyanurate foam in the presence of a blowing agent mixture comprising cyclopentane and a certain amount of other organic compounds as co-blowing agents, the saturated vapour pressure of said co-blowing agents in bar at  $T_{use}$  (v.p.) complying with the following equation (I): v.p.  $\geq 0.7 \text{ bar} \times T_{use}/298 \text{ }^{\circ}\text{K} \times C/100$  wherein C is the mole % of said co-blowing agent in gaseous form on the total blowing agent mixture in the gaseous phase after foaming and  $T_{use}$  is the temperature in  $^{\circ}\text{K}$  at which the foam is used.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## PROCESS FOR PREPARING RIGID POLYURETHANE FOAMS

### DESCRIPTION

This invention relates to processes for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, to foams prepared thereby, and to novel compositions useful in the process.

Rigid polyurethane and urethane-modified polyisocyanurate foams are in general prepared by reacting the appropriate polyisocyanate and isocyanate-reactive compound (usually a polyol) in the presence of a blowing agent. One use of such foams is as a thermal insulation medium as for example in the construction of refrigerated storage devices. The thermal insulating properties of rigid foams are dependent upon a number of factors including, for closed cell rigid foams, the cell size and the thermal conductivity of the contents of the cells.

A class of materials which has been widely used as blowing agent in the production of polyurethane and urethane-modified polyisocyanurate foams are the fully halogenated chlorofluorocarbons, and in particular trichlorofluoromethane (CFC-11). The exceptionally low thermal conductivity of these blowing agents, and in particular of CFC-11, has enabled the preparation of rigid foams having very effective insulation properties. Recent concern over the potential of chlorofluorocarbons to cause depletion of ozone in the atmosphere has led to an urgent need to develop reaction systems in which chlorofluorocarbon blowing agents are replaced by alternative materials which are environmentally acceptable and which also produce foams having the necessary properties for the many applications in which they are used.

A class of materials which have been used as alternative blowing agents with zero ozone depletion potential are alkanes and cycloalkanes such as n-pentane, isopentane and cyclopentane. Especially cyclopentane is preferred in view of its lower thermal conductivity. The use of cyclopentane as blowing agent in rigid polyurethane or urethane-modified polyisocyanurate foams is described in US Patent No. 5096933 and further in US Patent No. 5114986, US Patent No. 5166182, US Patent No. 4795763, US Patent No. 4898893, US Patent No. 5026502, European Patent Application No. 389011 and PCT Patent Application No. 92/16573.

A disadvantage of rigid polyurethane or urethane-modified polyisocyanurate foams blown with cyclopentane is their poor dimensional stability especially at temperatures below 20°C: a freshly made foam shows substantial shrinking

within the next 24 hours and also within the following weeks. Further the aged thermal insulation properties (this is the thermal insulation loss with time) of such foams is unsatisfactory, particularly at lower temperatures such as 10°C which is the average temperature of a refrigerator and especially at -10°C which is the average temperature of a freezer.

It is an object of the present invention to provide cyclopentane blown rigid polyurethane or urethane-modified polyisocyanurate foams having improved dimensional stabilities.

It is a further object of the present invention to provide cyclopentane blown rigid polyurethane or urethane-modified polyisocyanurate foams having improved aged thermal insulation properties.

Another further object of the present invention is to provide cyclopentane blown rigid polyurethane or urethane-modified polyisocyanurate foams having improved dimensional stabilities and improved aged thermal insulation properties without detrimentally affecting the initial thermal insulation of the foam.

These objects are met by using in the process of making rigid polyurethane or urethane-modified polyisocyanurate foams from polyisocyanates and isocyanate-reactive components besides cyclopentane as blowing agent certain amounts of other organic compounds as co-blowing agents, the saturated vapour pressure of said co-blowing agents in bar at  $T_{use}$  (v.p.) complying with the following equation (I)

$$v.p. \geq 0.7 \text{ bar} \times \frac{T_{use}}{298^\circ\text{K}} \times \frac{C}{100} \quad (\text{I})$$

wherein C is the mole % of said compound in gaseous form on the total blowing agent mixture in the gaseous phase after foaming and  $T_{use}$  is the temperature in °K at which the foam is used.

The saturated vapour pressure at  $T_{use}$  can be calculated from the boiling point of the co-blowing agent, its molecular heat of evaporation and  $T_{use}$  by using the Clausius-Clapeyron equation.

C, the mole % of the co-blowing agent on the total gaseous blowing agent mixture after foaming is determined assuming that no condensation of the blowing agent mixture in the foam cells takes place.

According to the present invention cyclopentane is used in combination with one or more other organic co-blowing agents the saturated vapour pressure of each of said co-blowing agents complying with the above equation (I).

Preferred classes of compounds for use as co-blowing agent according to the present invention are (*cyclo*)alkanes, hydrofluorocarbons, hydrochlorofluorocarbons, fluorocarbons, fluorinated ethers, alkenes, alkynes and noble gases. Especially preferred classes are alkanes and hydrofluorocarbons.

Examples of suitable (*cyclo*)alkanes for use according to the present invention include isopentane, n-pentane, neopentane, n-butane, cyclobutane, methylcyclobutane, isobutane, propane, cyclopropane, methylcyclopropane, n-hexane, 3-methylpentane, 2-methylpentane, cyclohexane, methylcyclopentane, n-heptane, 2-methylheptane, 3-ethylpentane, 2,2,3-trimethylbutane, 2,2-dimethylpentane, cycloheptane, methylcyclohexane and 2,3-dimethylbutane.

Examples of suitable hydrofluorocarbons for use according to the present invention include 1,1,1,2-tetrafluoroethane (HFC 134a), 1,1,1,4,4,4-hexafluorobutane (HFC 356), pentafluoroethane (HFC 125), 1,1-difluoroethane (HFC 152a), trifluoromethane (HFC 23), difluoromethane (HFC 32), trifluoroethane (HFC 143) and fluoromethane.

Examples of suitable hydrochlorofluorocarbons for use according to the present invention include chlorodifluoromethane (HCFC 22), 1-chloro-1,1-difluoroethane (HCFC 142b), 1,1,1-trifluoro-2,2-dichloroethane (HCFC 123) and dichlorofluoromethane (HCFC 21).

Examples of suitable fluorocarbons for use according to the present invention include perfluoromethane (R 14), perfluorocyclobutane, perfluorobutane, perfluoroethane and perfluoropropane.

Examples of suitable fluorinated ethers for use according to the present invention include bis-(trifluoromethyl) ether, trifluoromethyl difluoromethyl ether, methyl fluoromethyl ether, methyl trifluoromethyl ether, bis-(difluoromethyl) ether, fluoromethyl difluoromethyl ether, methyl difluoromethyl ether, bis-(fluoromethyl) ether, 2,2,2-trifluoroethyl difluoromethyl ether, pentafluoroethyl trifluoromethyl ether, pentafluoroethyl difluoromethyl ether, 1,1,2,2-tetrafluoroethyl difluoromethyl ether, 1,2,2,2-tetrafluoroethyl fluoromethyl ether, 1,2,2-trifluoroethyl difluoromethyl ether, 1,1-difluoroethyl methyl ether and 1,1,1,3,3-hexafluoroprop-2-yl fluoromethyl ether.

Examples of suitable alkenes for use according to the present invention include ethylene, propylene, 1-butene, 2-butene, propadiene, butadiene and

methylbutene.

Examples of suitable alkynes for use according to the present invention include acetylene and methylacetylene.

Examples of suitable noble gases for use according to the present invention include krypton, argon and xenon.

Preferred compounds for use as co-blown agents according to the present invention are isopentane, n-pentane and HFC 134a and a particularly preferred compound is isopentane.

By using compounds of which the saturated vapour pressure complies with the above equation (I) as blowing agents in addition to cyclopentane, rigid polyurethane foams are obtained that show improved dimensional stability at  $T_{use}$  compared to foams blown with cyclopentane alone.

Thus for example by using isopentane in an amount up to 75 mole % of the gaseous blowing agent mixture in addition to cyclopentane, foams with improved dimensional stability at 10°C (average temperature at which a rigid polyurethane foam is used in refrigeration) are obtained. Similarly by using n-pentane in an amount up to 55 mole % of the gaseous blowing agent mixture in addition to cyclopentane, foams with improved dimensional stability at 10°C are obtained.

According to a preferred embodiment of the present invention water or other carbon dioxide-evolving compounds are used together with the blowing agent mixture according to the present invention. Water is usually added to improve the flow of the reaction mixture. Where water is used as chemical co-blown agent typical amounts are in the range from 0.5 to 3 % by weight based on the isocyanate-reactive compound.

The optimum molar ratio cyclopentane/co-blowing agent according to the present invention will therefore depend not only on  $T_{use}$  and the vapour pressure of the co-blowing agent but also on the free rise density and on the amount of water that is used.

The optimum molar ratio cyclopentane/isopentane for a polyurethane foam with a free rise density of 22 kg/m<sup>3</sup> and a water amount of 0.5 pbw on the isocyanate-reactive component is between 15/85 and 40/60 for  $T_{use}$  being 10°C and between 15/85 and 65/35 for  $T_{use}$  being -10°C. The optimum molar ratio

cyclopentane/isopentane for a polyurethane foam with a free rise density of 22 kg/m<sup>3</sup> and a water amount of 2 pbw on the isocyanate-reactive component is between 5/95 and 45/55 for T<sub>use</sub> being 10°C and between 20/80 and 50/50 for T<sub>use</sub> being -10°C. The optimum molar ratio cyclopentane/isopentane for a polyurethane foam with a free rise density of 22 kg/m<sup>3</sup> and a water amount of 3 pbw on the isocyanate-reactive component is between 5/95 and 75/25 for T<sub>use</sub> being 10°C and between 25/75 and 35/65 for T<sub>use</sub> being -10°C.

In addition to the dimensional stability of the foams obtained by using the blowing agent mixture according to the present invention the aged thermal insulation properties of such foams can be improved. This will depend on the diffusion characteristics and thermal insulation properties of the co-blowing agent. The optimal amount of the co-blowing agent will therefore also depend on these characteristics of the co-blowing agent.

In particular when certain amounts of isopentane or n-pentane are used in combination with cyclopentane as blowing agent, rigid polyurethane or urethane-modified polyisocyanurate foams are obtained with improved dimensional stability and improved aged thermal insulation properties compared to foams blown with cyclopentane alone. And surprisingly the initial thermal conductivity of said cyclopentane/isopentane or n-pentane blown foams is not significantly higher than the initial thermal conductivity of cyclopentane blown foams although the thermal insulation properties of isopentane and n-pentane are worse than the thermal insulation properties of cyclopentane. Further isopentane and n-pentane are considerably cheaper than cyclopentane. Thus by substituting part of the cyclopentane by the worse insulating materials isopentane or n-pentane foams are obtained with comparable initial thermal conductivity at lower cost and moreover the dimensional stability and the aged thermal insulation properties of such foams are improved compared to cyclopentane blown foams.

When isopentane or n-pentane is used in combination with cyclopentane the preferred molar ratio cyclopentane/iso- or n-pentane for T<sub>use</sub> being 10°C is between 90/10 and 30/70, preferably between 80/20 and 30/70 and more preferably between 70/30 and 40/60 and most preferably between 65/35 and 45/55 in order to obtain rigid polyurethane foams with improved dimensional stability and improved aged thermal insulation properties without significantly affecting the initial thermal conductivity.

In addition to the cyclopentane and the co-blowing agent(s) complying with the above equation (I) the blowing agent mixture according to the present

invention may also contain up to 20 mole % of the total blowing agent mixture of other physical blowing agents not complying with equation (I). This is especially true since the commercially available cyclopentane is usually a technical (70 to 80 %) grade comprising small amounts of other hydrocarbons rather than a pure grade.

Suitable physical blowing agents include those well known and described in the art, for example hydrocarbons, dialkyl ethers, alkyl alkanoates, aliphatic and cycloaliphatic hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, hydrochlorocarbons and fluorine-containing ethers.

The total quantity of blowing agent to be used in a reaction system for producing cellular polymeric materials will be readily determined by those skilled in the art, but will typically be from 2 to 25 % by weight based on the total reaction system.

In order to reduce the cell sizes of the foam and accordingly to improve the thermal insulation properties an inert, insoluble fluorinated compound may be used in the foam-forming process according to the present invention. Such inert, insoluble fluorinated compounds include any of those disclosed in US Patent No. 4981879; US Patent No. 5034424, US Patent No. 4972002 and European Patent Application No. 0508649. Certain of said inert, insoluble fluorinated compounds suitable for use in the process of the invention may themselves act as blowing agents under the conditions pertaining to the foam-forming reaction, particularly where their boiling point is lower than the exotherm temperature achieved by the reaction mixture.

Suitable organic polyisocyanates for use in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4- and 2,6-isomers and mixtures thereof, 1,5-naphthalene diisocyanate and 1,4-diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include the aliphatic diisocyanates such as isophorone diisocyanate, 1,6-diisocyanatohexane and 4,4'-diisocyanatodicyclohexylmethane.

Polyfunctional isocyanate-reactive compositions with which the polyisocyanate composition can be reacted to form rigid polyurethane or urethane-modified

polyisocyanurate foams include any of those known in the art for that purpose. Of particular importance for the preparation of rigid foams are polyols and polyol mixtures having average hydroxyl numbers of from 300 to 1000, especially from 300 to 700 mg KOH/g, and hydroxyl functionalities of from 2 to 8, especially from 3 to 8. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule. Suitable initiators include: polyols, for example glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose; polyamines, for example ethylene diamine, tolylene diamine, diaminodiphenylmethane and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Preferred initiators for use in the present invention are diaminodiphenylmethane and polymethylene polyphenylene polyamines. Foams made from polyols initiated by these compounds show improved dimensional stability compared to foams made from polyols initiated by other conventional compounds such as sucrose. Other suitable polymeric polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or polycarboxylic acids. Still further suitable polymeric polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes.

The quantities of the polyisocyanate compositions and the polyfunctional isocyanate-reactive compositions to be reacted will depend upon the nature of the rigid polyurethane or urethane-modified polyisocyanurate foam to be produced and will be readily determined by those skilled in the art.

In addition to the polyisocyanate and polyfunctional isocyanate-reactive compositions and the blowing agent mixture of the present invention, the foam-forming reaction mixture will commonly contain one or more other auxiliaries or additives conventional to formulations for the production of rigid polyurethane and urethane-modified polyisocyanurate foams. Such optional additives include crosslinking agents, for examples low molecular weight polyols such as triethanolamine, foam-stabilising agents or surfactants, for example siloxane-oxyalkylene copolymers, urethane catalysts, for example tin compounds such as stannous octoate or dibutyltin dilaurate or tertiary amines such as dimethylcyclohexylamine or triethylene diamine, and fire retardants, for example halogenated alkyl phosphates such as tris chloropropyl phosphate.

In operating the process for making rigid foams according to the invention,

the known one-shot, prepolymer or semi-prepolymer techniques may be used together with conventional mixing methods and the rigid foam may be produced in the form of slabstock, mouldings, cavity fillings, sprayed foam, frothed foam or laminates with other materials such as hardboard, plasterboard, plastics, paper or metal.

It is convenient in many applications to provide the components for polyurethane production in pre-blended formulations based on each of the primary polyisocyanate and isocyanate-reactive components. In particular, many reaction systems employ a polyisocyanate-reactive composition which contains the major additives such as the blowing agent and the catalyst in addition to the polyisocyanate-reactive component or components.

Therefore the present invention also provides a polyisocyanate composition or a polyisocyanate-reactive composition comprising as blowing agents cyclopentane and certain amounts of other organic compounds of which the saturated vapour pressure at  $T_{use}$  complies with the following equation (I)

$$v.p. \geq \frac{0.7 \text{ bar} \times T_{use}}{298^\circ\text{K}} \times \frac{C}{100} \quad (\text{I})$$

wherein v.p. is the saturated vapour pressure of said compound in bar at  $T_{use}$ , C is the mole % of said compound in gaseous form on the total blowing agent mixture in the gaseous phase after foaming and  $T_{use}$  is the temperature in  $^\circ\text{K}$  at which the foam is used.

The various aspects of this invention are illustrated, but not limited by the following examples.

The following formulation and reaction components are referred to in the examples:

Daltolac XR159: A polyether polyol from Imperial Chemical Industries  
Daltolac XR144: A polyether polyol from Imperial Chemical Industries  
Daltolac R 180: A polyether polyol from Imperial Chemical Industries  
Daltolac R 260: A polyether polyol from Imperial Chemical Industries  
Catalyst SFC: A tertiary amine catalyst from Imperial Chemical Industries  
Niax A1: A tertiary amine catalyst from Union Carbide  
DC 193: A silicone surfactant from Air Products  
RS 201: A surfactant from Union Carbide  
Cyclopentane A: A 78 % grade cyclopentane from Exxon  
Cyclopentane B: A 98 % grade cyclopentane from Shell  
Isopentane: A 98 % grade isopentane from Janssen  
Suprasec DNR: A polymeric MDI from Imperial Chemical Industries

Daltolac and Suprasec are trademarks from Imperial Chemical Industries PLC.

EXAMPLE 1

Rigid polyurethane foams were prepared from the starting components given in table 1 (amounts in pbw). Characteristics of the foam-forming reaction profiles, density and thermal conductivity characteristics were determined. Table 1 records the cream time (time taken from the mixing of the two reactive compositions till the onset of the blowing reaction), the string time (time taken for the reaction mixture to reach the transition point from fluid to cross-linked mass) and the end of rise time, all assessed visually. Further the free rise density (density of the foam after free expansion) and the core density (measured according to DIN 53420 standard) of the foam is recorded. Thermal conductivity properties (lambda values) at a mean temperature of 10°C were determined initially, after 6 days at 70°C, after 3 weeks at 70°C and after 5 weeks at 70°C.

FOAM		Comp_1	2	3	4	5	6
XR 159	pbw	58.0	58.0	58.0	58.0	58.0	58.0
XR 144	pbw	42.0	42.0	42.0	42.0	42.0	42.0
SFC	pbw	1.4	1.4	1.4	1.4	1.4	1.4
Niax A1	pbw	0.1	0.1	0.1	0.1	0.1	0.1
DC 193	pbw	3.0	3.0	3.0	3.0	3.0	3.0
Water	pbw	2.0	2.0	2.0	2.0	2.0	2.0
Cyclopentane A	pbw	15.0	13.5	12.0	10.5	9.0	7.5
Isopentane	pbw	-	1.5	3.0	4.5	6.0	7.5
DNR	pbw	140.0	140.0	140.0	140.0	140.0	140.0

## Reaction Profile

Cream time	sec	10	10	10	10	10	10
String time	sec	54	54	55	56	56	56
End of rise time	sec	135	135	135	135	135	135
Free_rise_density	kg/m <sup>3</sup>	24.1	24.4	24.9	24.5	24.4	24.0
Thermal_Conductivity							
Core Density	kg/m <sup>3</sup>	28.25	27.75	28.45	28.75	29.0	29.3
Initial Lambda	mW/mK	21.2	21.6	21.9	21.9	21.85	21.8
Lambda 6d/70°C	mW/mK	24.9	25.3	25.25	24.35	24.6	24.45
Lambda Increase after 6d	mW/mK	+ 3.7	+ 3.7	+ 3.35	+ 2.45	+ 2.75	+ 2.65
Lambda 3w/70°C	mW/mK	26.85	26.95	26.8	26.3	26.15	25.85
Lambda Increase after 3w	mW/mK	+ 5.65	+ 5.35	+ 4.9	+ 4.4	+ 4.3	+ 4.05
Lambda 5w / 70°C	mW/mK	27.45	27.25	27.25	26.6	26.6	26.45
Lambda Increase after 5w	mW/mK	+ 6.25	+ 5.65	+ 5.35	+ 4.7	+ 4.75	+ 4.65

These results show that by using mixtures of cyclopentane and isopentane in molar ratios of cyclopentane/isopentane ranging from about 90/10 to 40/60 (foams 2 to 6) foams are obtained with improved aged thermal insulation properties without substantially affecting the initial thermal insulation compared to foams blown with cyclopentane alone (comparative foam 1).

#### EXAMPLE 2

Rigid polyurethane foams were prepared from the starting components given in table 2 (amounts in pbw).

The dimensional stability of the resulting foams at -20°C after 1 day and after 14 days was checked by measuring the variation in length, in width and in thickness (according to ISO 2796 standard).

The results are presented in table 2.

TABLE 2

<u>FOAM</u>		<u>Comp. 7</u>	<u>8</u>	<u>9</u>
R 180	pbw	85	85	85
R 260	pbw	15	15	15
SFC	pbw	3.5	3.5	3.5
Niax Al	pbw	0.2	0.2	0.2
Water	pbw	2.0	2.0	2.0
RS 201	pbw	3.0	3.0	3.0
Cyclopentane A	pbw	15.0	10.5	7.5
Isopentane	pbw	-	4.5	7.5
DNR	pbw	140	140	140
Core Density	kg/m <sup>3</sup>	27.5	28.1	27.4
<u>Dimensional stability</u> <u>after 1 day</u>				
length	%	- 1.06	- 3.54	- 0.09
width	%	- 1.07	3.42	0.18
thickness	%	0.76	0.53	0.63
<u>Dimensional stability</u> <u>after 14 days</u>				
length	%	- 4.60	- 0.96	- 0.44
width	%	- 2.16	- 1.19	0.06
thickness	%	0.43	0.62	- 0.18

These results show that by using mixtures of cyclopentane and isopentane foams are obtained with improved dimensional stabilities compared to foams blown with cyclopentane alone (comparative foam 7).

#### EXAMPLE 3

Rigid polyurethane foams were prepared from the starting components given in table 3 (amounts in pbw). Density and thermal conductivity characteristics were determined. Thermal conductivity properties (lambda values) were determined initially, after 1 week at 70°C, after 3 weeks at 70°C and after 5 weeks at 70°C.

TABLE 3

<u>FOAM</u>		<u>Comp 10</u>	<u>11</u>	<u>Comp 12</u>	<u>13</u>
XR 144	pbw	42.0	42.0	-	-
XR 159.	pbw	58.0	58.0	-	-
R 180	pbw	-	-	85	85
R 260	pbw	-	-	15	15
SFC	pbw	1.4	1.4	3.5	3.5
Niax A1	pbw	0.1	0.1	0.2	0.2
DC 193	pbw	3.0	3.0	-	-
RS 201	pbw	-	-	3.0	3.0
Water	pbw	2.0	2.0	2.0	2.0
Cyclopentane B	pbw	15.0	7.5	15.0	7.5
Isopentane	pbw	-	7.5	-	7.5
DNR	pbw	140.0	140.0	140.0	140.0
Core Density	kg/m <sup>3</sup>	34	29	35	31
Initial Lambda	mW/mK	21.1	21.5	21.5	22.1
Lambda 1w/70°C	mW/mK	23.9	24.5	25.9	26.6
Lambda increase after 1 w	mW/mK	2.8	3.0	4.4	4.5
Lambda 3w/70°C	mW/mK	26.0	26.1	27.4	27.4
Lambda increase after 3 w	mW/mK	4.9	4.6	5.9	5.3
Lambda 5w/70°C	mW/mK	27.5	26.4	27.5	27.1
Lambda increase after 5 w	mW/mK	6.4	4.9	6.0	5.0

## CLAIMS

1. Process for the preparation of a rigid polyurethane or urethane-modified polyisocyanurate foam by reaction of a polyisocyanate composition with a polyfunctional isocyanate-reactive composition under foam-forming conditions in the presence of a blowing agent mixture comprising cyclopentane, characterised in that said blowing agent mixture further comprises certain amounts of other organic compounds as co-blowing agents, the saturated vapour pressure of said co-blowing agents in bar at  $T_{use}$  (v.p.) complying with the following equation (I)

$$v.p. \geq \frac{0.7 \text{ bar} \times T_{use} \times C}{298^\circ\text{K} \quad 100} \quad (\text{I})$$

wherein C is the mole % of said co-blowing agent in gaseous form on the total blowing agent mixture in the gaseous phase after foaming and  $T_{use}$  is the temperature in °K at which the foam is used.

2. Process according to claim 1, wherein the co-blowing agent is an alkane or a cycloalkane or a hydrofluorocarbon.
3. Process according to claim 2, wherein the co-blowing agent is isopentane or n-pentane or 1,1,1,2-tetrafluoroethane.
4. Process according to any one of the preceding claims, wherein water is also present in amounts ranging from 0.5 to 3 % by weight based on the isocyanate-reactive compound.
5. Process according to claim 3, wherein the molar ratio cyclopentane/isopentane is between 90/10 and 30/70.
6. Process according to claim 5, wherein the molar ratio cyclopentane/isopentane is between 65/35 and 45/55.
7. Polyurethane or urethane-modified polyisocyanurate foam obtainable by the process defined in any one of claims 1 to 6.
8. Polyisocyanate-reactive composition containing a blowing agent mixture comprising cyclopentane, characterised in that said blowing agent mixture further comprises certain amount of other organic compounds as co-blowing agents, the saturated vapour pressure of said co-blowing agents in bar at  $T_{use}$  (v.p.) complying with the following equation (I)

$$v.p. \geq \frac{0.7 \text{ bar} \times T_{use}}{298^\circ\text{K}} \times \frac{C}{100} \quad (\text{I})$$

wherein C is the mole % of said co-blown agent in gaseous form on the total blowing agent mixture in the gaseous phase after foaming and  $T_{use}$  is the temperature in  $^\circ\text{K}$  at which the foam is used.

9. Polyisocyanate-reactive composition according to claim 8, wherein the co-blown agent is isopentane or n-pentane or 1,1,1,2-tetrafluoroethane.
10. Polyisocyanate-reactive composition according to claim 8 or 9, wherein said composition further comprises water in an amount ranging from 0.5 to 3 % by weight based on the isocyanate-reactive compound.
11. Polyisocyanate-reactive composition according to claim 9, wherein the molar ratio cyclopentane/isopentane is between 90/10 and 30/70.
12. Polyisocyanate-reactive composition according to claim 11, wherein the molar ratio cyclopentane/isopentane is between 65/35 and 45/55.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 C08J9/14 //C08L75:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 5 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 819 547 (PILLAR & AL.) 25 June 1974 see claims 1,4 ---	1-12
A	EP,A,0 421 269 (BASF) 10 April 1991 see page 7, column 11, line 40 - page 7, column 12, line 3 see claims 1-10 ---	1-12
P,X	EP,A,0 551 636 (BASF) 21 July 1993 see claims 1-8 -----	1-12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

1

Date of the actual completion of the international search

29 April 1994

Date of mailing of the international search report

25.05.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+ 31-70) 340-3016

Authorized officer

Oudot, R

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3819547	25-06-74	BE-A-	817426	04-11-74
		CA-A-	1021899	29-11-77
		DE-A, B	2430623	28-05-75
		FR-A, B	2236914	16-01-75
		GB-A-	1460061	31-12-76
		JP-C-	955620	31-05-79
		JP-A-	50043170	18-04-75
		JP-B-	52026775	15-07-77
		NL-A-	7409120	13-01-75
		SE-B-	395902	29-08-77
		SE-A-	7408638	10-01-75
EP-A-0421269	10-04-91	DE-A-	3933335	11-04-91
		CA-A-	2024714	07-04-91
		JP-A-	3152160	28-06-91
		US-A-	5096933	17-03-92
EP-A-0551636	21-07-93	DE-A-	4200558	15-07-93
		CA-A-	2086997	12-07-93
		US-A-	5290823	01-03-94